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J. Solis, J. Siegel, C. N. Afonso, J. Jimenez, and C. García

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Supercooling and structural relaxation in amorphous Ge films under pulsed laser irradiation

J. Solis,^{a)} J. Siegel, and C. N. Afonso
Instituto de Optica, CSIC, C/Serrano 121, 28006-Madrid, Spain

J. Jimenez and C. García
Dpto. de Física de la Materia Condensada, Cristalografía y Mineralogía. Universidad de Valladolid, 47011-Valladolid, Spain

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Melting and rapid solidification has been induced in amorphous Ge films by irradiation with nano- and picosecond laser pulses. The degree of structural relaxation of the rapidly solidified amorphous material has been investigated both by determining the minimum fluence required for surface melting and by means of Raman spectroscopy. The results evidence that the degree of relaxation of the rapidly solidified material is controlled by several parameters such as the duration and fluence of the laser pulse, and the thermal conductivity of the substrate, all of them affecting the supercooling prior to solidification. It is demonstrated that both relaxation and derelaxation can be induced if the above mentioned parameters are properly selected. The degree of relaxation is observed to decrease as the supercooling increases. © 1997 American Institute of Physics. [S0021-8979(97)05113-X]

INTRODUCTION

The structure of amorphous Si (*a*-Si) and Ge (*a*-Ge) is reasonably well understood and is generally considered to be a continuous random network¹ in which the short range order within the amorphous phase can range from a minimum to a maximum level through a continuum of different thermodynamic states.^{2,3} The evolution of the amorphous phase to a state of lower energy is usually referred to as structural relaxation and this phenomenon has received considerable attention during the last years. The relaxation mechanisms⁴ and their relation to the presence of defects in the amorphous phase are nevertheless controversial.⁵⁻⁷

The influence of the degree of relaxation on different physical properties of *a*-Si and *a*-Ge is still actively investigated. The continuous transition from the maximally disordered (fully derelaxed) to the minimally disordered (fully relaxed) amorphous material is accompanied by changes in the optical⁸ and electrical⁹ properties, density,¹⁰ viscosity,¹¹ diffusivity,¹² thermal conductivity,^{13,14} and vibrational properties.¹⁵ The determination of the melting temperature of fully relaxed and fully derelaxed *a*-Si and *a*-Ge has been the subject of several studies^{13,16,17} due to the importance of this parameter for the comprehension of the thermodynamics of the amorphous-liquid and amorphous-crystalline phase transitions in both materials.

Structural relaxation has been induced in most cases by thermal annealing of bulk ion implanted amorphous samples while derelaxation has been observed upon low dose ion implantation of a previously relaxed material.^{8,18} Laser irradiation has been also demonstrated to be an effective means to promote relaxation both in bulk samples¹⁹ and thin films¹⁷ but only very recently, derelaxation phenomena have been observed in the latter as a consequence of melting and rapid

solidification induced by ultrashort laser pulses.²⁰ The relation between the relaxation enthalpy and the quenching rate observed in metallic glasses,²¹ as well as *ab initio* molecular dynamics calculations about the structure and properties of quenched *a*-Si²² also suggest that laser induced rapid solidification of thin films may provide an adequate means to modify the state of relaxation of *a*-Ge or *a*-Si in a controllable way.

This work reports a study of structural relaxation phenomena induced in *a*-Ge films by pulsed laser induced rapid solidification. In order to investigate the relation between the solidification conditions and the degree of relaxation achieved, the behavior of *a*-Ge films on substrates with different thermal properties under irradiation with ns and ps laser pulses has been analyzed. The degree of structural relaxation of the irradiated material has been studied by determining the minimum fluence required for inducing surface melting^{13,17} and by means of Raman spectroscopy.¹⁵ The results indicate that the degree of relaxation of the rapidly solidified material can be either lower or higher than that of the as-deposited one depending on the supercooling achieved prior to solidification.

EXPERIMENT

The samples used in this study are 50-nm-thick *a*-Ge films grown by dc sputtering. The films are grown from a (99.999%) Ge target using an Ar operating pressure of 4×10^{-3} Torr in a vacuum system with a residual pressure of 3×10^{-6} Torr. The substrates, either glass or Si(100) wafers covered by their native oxide, are held at room temperature during the deposition. The optical and structural characterization of films grown under similar conditions has been reported elsewhere²³ showing that the as-deposited material is a very dense amorphous film.

^{a)}Electronic mail: iodjs37@pinar1.csic.es

Surface melting and rapid solidification is induced by either 10 ps laser pulses at 583 nm or 12 ns laser pulses at 193 nm. The former are provided by a synchronously pumped mode-locked dye laser (Rhodamine 6G) whose output is amplified by a pulsed dye amplifier (Sulforhodamine B) pumped by a frequency doubled Nd-YAG laser. The amplified beam has a gaussian elliptical spatial profile and is spatially filtered before being focused on the sample to a size of $\approx 600 \mu\text{m}$ ($1/e$ diameter), leading to fluences in the 0–200 mJ/cm^2 range. The nanosecond laser pulses are provided by an ArF excimer laser. The use of a beam homogenizer leads to a homogeneously illuminated spot of $4 \times 4 \text{ mm}$ at the sample site. In this case, the fluences are in the 0–350 mJ/cm^2 range. The determination of the absolute fluence values at the sample site is performed within 10% and 5% for ps and ns laser pulses, respectively, while the comparison of the relative fluences of two pulses of the same duration can be done with an accuracy close to 2%. For both pulse durations, the evolution of the sample reflectivity is measured in real time by means of a HeNe probe laser beam (632.8 nm) focused on the center of the irradiated region to a size of $\approx 50 \mu\text{m}$ ($1/e$ diameter), which guarantees that the reflectivity is measured over a homogeneously irradiated area. After each laser pulse, the sample is moved to a fresh region. Further details are reported elsewhere.^{24,25}

After irradiation, the samples are inspected by optical microscopy and their structure is characterized by means of Raman spectroscopy in micro-Raman configuration.²⁶ The Raman measurements were carried out with a DILOR XY Raman spectrometer attached to a metallographic microscope for excitation and scattered light collection. The excitation beam is delivered by an Ar^+ ion laser at 514 nm. In order to avoid the presence of both spectral broadening and/or annealing of the surface due to laser induced heating, the power of the excitation beam is kept low enough (a few mW) and the beam is slightly defocused leading to a spatial resolution of a few μm .

RESULTS

Figure 1 shows two representative real time reflectivity (RTR) transients obtained upon irradiation of as-deposited a -Ge films on glass substrates with 10 ps laser pulses. The absorption of the irradiation pulse leads to a sharp reflectivity increase up to a maximum. For fluences above a certain threshold value, the reflectivity at the maximum is above that of the solid material at the melting temperature,¹⁷ thus indicating that surface melting has been induced. Above this threshold and for fluences below $\approx 50 \text{ mJ}/\text{cm}^2$, [transient (a) in Fig. 1], the maximum is followed first by an abrupt decrease and, subsequently, by a smoother decay. The final reflectivity level is reached approximately after 200 ns (not shown in the figure) and its value is similar to that of the as-deposited material, in agreement with the reamorphization of the molten and solidified layer. This interpretation was confirmed by means of Raman spectroscopy. For fluences above $\approx 50 \text{ mJ}/\text{cm}^2$, [transient (b) in Fig. 1], the decrease after the maximum shows a shoulder followed by an additional decrease at a slower rate. The final reflectivity value observed in this case is always lower than the initial one and

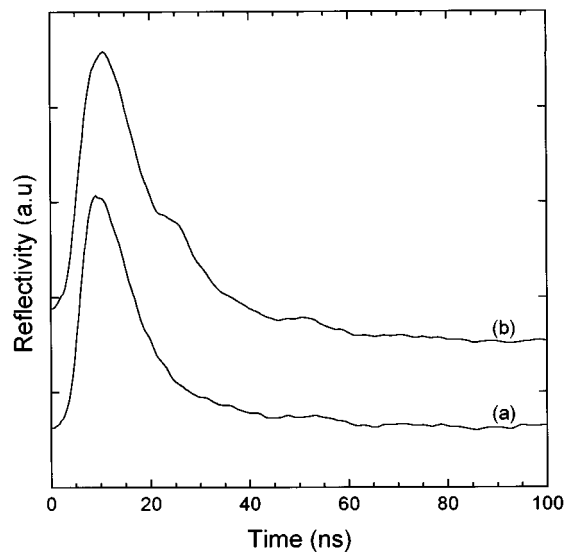


FIG. 1. Real time reflectivity transients obtained in as-deposited a -Ge films on glass substrates upon irradiation with a single ps laser pulse. The corresponding fluences are (a) 42 and (b) 60 mJ/cm^2 . The zero of the horizontal scale corresponds to the temporal position of the irradiation pulse.

Raman spectroscopy indicates the formation of polycrystalline material.²⁷ This type of transient has been reported earlier and has been related to recalescence and crystalline phase formation during solidification²⁸ as discussed elsewhere.²⁵

The transients obtained upon ps pulse irradiation of films on Si substrates are similar to the transient (a) in Fig. 1, but in a slightly compressed time scale. Neither recalescence nor crystalline phase formation is observed in these films even for ps pulse fluences up to the ablation threshold. The same applies upon ns laser pulse irradiation of the films on Si but obviously, the temporal width of the transients is much bigger. In the films on glass substrates, crystallization is always induced by irradiation with ns pulses of fluences above the melting threshold.

Figure 2(a) shows the evolution of the maximum transient reflectivity value (R_{max}) induced upon irradiation with ps laser pulses in films on glass. The same figure also includes the evolution of the final reflectivity (R_{fin}) of the surface. The reflectivity values have been normalized to the reflectivity of the as-deposited material according to the formula $R_n = (R - R_0)/R_0$, where R_n denotes the normalized value, R is either R_{max} or R_{fin} , and R_0 is the reflectivity of the as-deposited material at room temperature. Since the normalized reflectivity value of the amorphous solid at the melting temperature is 0.14–0.15,¹⁷ the presence of normalized R_{max} values above this number indicates that surface melting is induced. The further increase observed for high fluences is related to the thickness of the molten layer.²⁵ The final reflectivity of the surface is similar to the initial one for fluences below $\approx 50 \text{ mJ}/\text{cm}^2$. For higher fluences, when the shoulder is observed in the transients [(b), Fig. 1], R_{fin} is clearly smaller than R_0 due to the formation of polycrystalline material upon solidification.

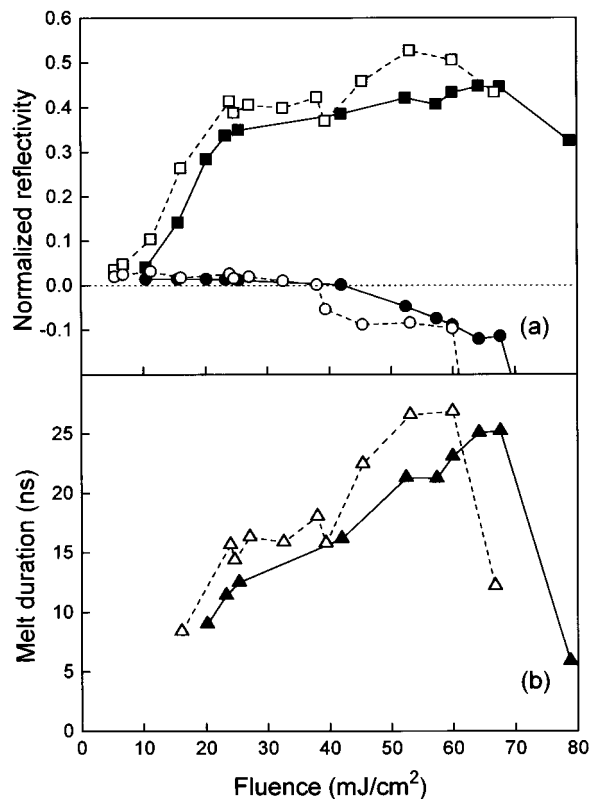


FIG. 2. Normalized (■) maximum transient reflectivity and (●) final reflectivity, and (▲) melt duration as a function of laser fluence measured in as-deposited *a*-Ge films on glass substrates upon irradiation with a single ps laser pulse. The open symbols correspond to the same parameters measured in a sample that was pretreated with a ps laser pulse at a fluence of 22 mJ/cm².

The melt duration has been obtained from the reflectivity transients as the time interval during which the reflectivity of the surface remains above that of the solid material at the melting temperature. The corresponding values have been plotted as a function of the laser pulse fluence in Fig. 2(b). The threshold fluence required for surface melting (from now on referred to as melting threshold) is easily determined from this curve as the fluence at which the first nonzero melt duration value is observed.^{29,30} The melting threshold is 20 mJ/cm² in this case. The melt duration increases with the pulse fluence until the ablation threshold is reached at ≈ 70 mJ/cm². The melting threshold of films on different substrates under either ns or ps laser pulse irradiation was determined in the same way. The value obtained for films on Si under ps laser pulses is equal to the one observed in the films on glass within the experiment resolution. Upon irradiation with ns laser pulses, the observed melting threshold values are, respectively, 45 and 60 mJ/cm² for the films on glass and on Si substrates.

In order to analyze the degree of relaxation of the amorphous material obtained upon melting and rapid solidification, the melting threshold for ps laser pulses¹³ was measured in regions that had been previously irradiated with a single laser pulse (either ps or ns) with a fluence above the melting threshold. Thus each selected region is irradiated by two pulses, the first one having a fixed fluence. The second one

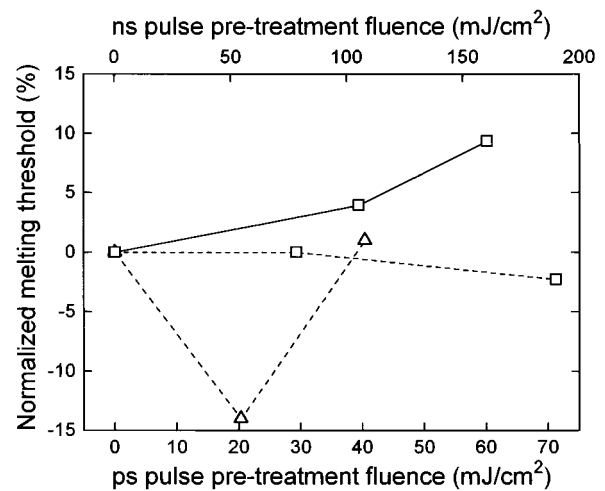


FIG. 3. Normalized melting threshold of *a*-Ge films (Δ) on glass and (\square) on Si substrates pretreated with ps (dashed lines) and ns (solid line) laser pulses vs the pretreatment pulse fluence.

has a variable fluence in order to determine the evolution of the melt duration versus fluence in the material which has been transformed by the first pulse. The latter will be referred to from now on as pretreated material. Figure 2 also includes the evolution versus fluence of R_{\max} , R_{fin} , and the melt duration in the material pretreated with one ps laser pulse at a fluence of 22 mJ/cm². It can be seen that the curves corresponding to the pretreated material are clearly shifted to the lower fluences when compared to the curves of the as-deposited material. In particular, the melting threshold of the pretreated material is 15% lower than that of the as-deposited one (17 against 20 mJ/cm²).

The evolution of the melting threshold for ps pulses has been plotted as a function of the pretreatment pulse fluence in Fig. 3. The figure includes results obtained both for samples on glass and Si substrates that were pretreated with a ps laser pulse and for films on Si substrates pretreated with a ns laser pulse. Results for ns pulse pretreatment of films on glass are not included in the plot since ns laser pulse induced melting in these films always leads to crystallization. The quoted values have been normalized as $100 \times (E - E_{\text{ad}})/E_{\text{ad}}$, where E and E_{ad} denote the melting threshold for ps pulses of the pretreated and the as-deposited material, respectively. The latter has been plotted in the figure as the point at a zero pretreatment fluence. Very different effects are observed in the figure depending on the pulse duration and fluence and the nature of the substrate. For the case of ps laser pulse pretreatment of films on glass, the melting threshold is observed to decrease well below the value of the as-deposited material for a pretreatment fluence just above the melting threshold. If the pretreatment pulse fluence is increased up to a value close to the recalescence (crystallization) threshold, the melting threshold recovers a value similar to that of the as-deposited material. The threshold remains nearly unchanged for the films on Si, and only for the highest pretreatment fluence, a slight decrease in the threshold can be observed. In the case of ns laser pulse pretreatment of films on Si substrates, the melting threshold is

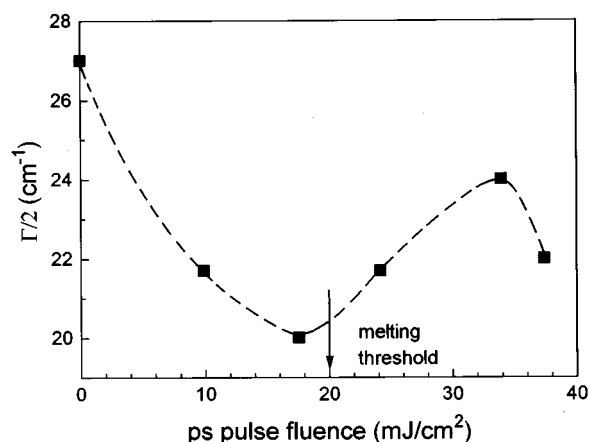


FIG. 4. Evolution of the high frequency half-width of the transverse optic phonon band of a -Ge at 270 cm^{-1} ($\Gamma/2$) in a -Ge films on glass substrates irradiated with a single ps laser pulse vs the laser pulse fluence. The zero of the horizontal scale corresponds to the value measured in the as-deposited material. The arrow indicates the minimum pulse fluence required for surface melting and the dashed lines are a guide to the eye.

always higher than that of the as-deposited material and increases with the pretreatment pulse fluence.

The degree of relaxation of the amorphous material obtained upon melting and rapid solidification was also investigated by means of Raman spectroscopy. It is well known that the high frequency half-width ($\Gamma/2$) of the transverse optic (TO) phonon band of the Raman spectrum of a -Ge (at 275 cm^{-1}) is directly related to the average bond angle distortion ($\Delta\theta$) in the amorphous material.^{31–33} Figure 4 shows the values of $\Gamma/2$ measured in films on glass substrates irradiated by a single ps pulse at several fluences below the recalescence threshold. The value quoted for zero fluence corresponds to that of the as-deposited material. It can be clearly seen that $\Gamma/2$ decreases with fluence reaching a minimum for a fluence close to the melting threshold. The value of $\Gamma/2$ increases then for higher fluences and reaches a maximum which is followed by a decreasing behavior as the fluence approaches the recalescence threshold. Figure 5 includes the results for films on Si substrates also under ps pulses, the global evolution being very similar to that observed for the films on glass: $\Gamma/2$ shows a minimum in the vicinity of the melting threshold and a maximum for a certain fluence above it, which is followed by a decreasing behavior for higher fluences.

DISCUSSION

The present results show clear differences between the melting threshold measured in the as-deposited films and in the laser pretreated material. Such differences depend both on the thermal conductivity of the substrate and the laser pretreatment conditions and should be correlated to changes in the degree of relaxation of the material undergoing melting and rapid solidification. It has been reported that the melting threshold for ps laser pulses in fully relaxed a -Si can be up to 30% higher than in the fully derelaxed material¹³

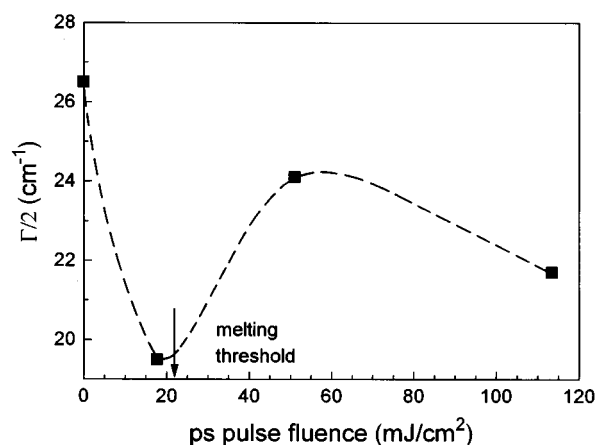


FIG. 5. As in Fig. 4, but for a -Ge films on Si substrates irradiated with ps laser pulses.

while the melting threshold for ns laser pulses in a -Ge films has been observed to increase up to 100% upon relaxation.¹⁷ The higher melting threshold values in the relaxed material have been related to an increase of both the thermal conductivity and the melting temperature of the amorphous phase.^{13,17,14} In our case, the a -Ge films on Si substrates pretreated with a ns laser pulse above the melting threshold (60 mJ/cm^2), have a melting threshold for ps pulses clearly higher than that observed in the as-deposited material (Fig. 3), in complete agreement with the results provided in Ref. 17. The value there reported for $\Gamma/2$ in the material irradiated with ns laser pulses was $\approx 3\text{ cm}^{-1}$ lower than in the as-deposited one, consistently with a reduction in the average bond angle distortion.³¹ The observed behavior indicates therefore that the material obtained upon ns laser pulse pretreatment of films on Si is more relaxed than the as-deposited one.

However, a very different behavior is observed upon ps pulse pretreatment (Fig. 3). In the films on Si substrates, the melting threshold seems to decrease slightly as the pretreatment pulse fluence is increased. The decrease is considerably higher (15%) in the films on glass substrates pretreated with a ps pulse at a fluence just above the melting threshold. This result, a decrease in the melting threshold upon irradiation with a ps laser pulse, is consistent with the formation of a material less relaxed than the as-deposited one (derelaxed state). It has been shown that the solidification scenario can change drastically when reducing the pulse duration from ns to ps, solidification upon ps laser pulse irradiation occurring at larger supercoolings (around 600 K^{25}). The present results thus support the existence of a direct relation between the degree of structural relaxation of the rapidly solidified material and the supercooling achieved prior to solidification; the lower the supercooling the higher the degree of relaxation. The results obtained upon irradiation with ns laser pulses further support this interpretation since the melting threshold (and thus the degree of relaxation) of the pretreated material increases with the fluence and it is well known that the supercooling decreases for increasing fluences. The precise mechanism responsible for the derelaxation effects observed

in the Ge films solidified at large supercoolings cannot be established from the present experimental results and its determination is beyond the scope of this work. However, it has been recently pointed out⁷ that structural relaxation processes in rapidly solidified Si at very large supercoolings might show strong peculiarities related to the possible existence of a glass transition for supercoolings of ≈ 700 K,³⁴ a value which is close to the one achieved in our experimental conditions in the films irradiated with ps pulses. This glass transition would quench the structure of the liquid, preventing further ordering upon solidification thus promoting the formation of the derelaxed material. Metallic glasses are known to exhibit a similar relation between the free energy of the rapidly solidified material (degree of relaxation) and the supercooling prior to solidification,²¹ but this had not been experimentally demonstrated so far in rapidly solidified amorphous semiconductors.

The comparison of the melting threshold (Fig. 3) of the films on glass substrates pretreated with a pulse fluence just above the melting threshold and the values of $\Gamma/2$ obtained from Raman measurements shown in Fig. 4 leads however to an apparent contradiction, since the observed value of $\Gamma/2$ is below the one measured in the as-deposited material and is thus consistent with a relaxation process. Similar discrepancies between Raman spectroscopy observations and melting threshold measurements have been earlier reported in laser irradiated ion-doped *a*-Si layers and have been explained in terms of the differences between the Raman probe penetration depth and the thickness of the transformed layer.¹³ In our case, the Raman beam probes a volume of material with a thickness of 30–40 nm.³⁵ The maximum transient reflectivity values observed in the films on glass upon ps laser pulse irradiation [Fig. 2(a)] are consistent with melt depths not bigger than 20 nm even for fluences close to the recalescence threshold.²⁵ This would explain the apparent disagreement between the melting threshold measurements and the Raman observations upon ps pulse irradiation. Upon irradiation with ns laser pulses, the melt depth at the fluences used is about 40 nm³⁶ and therefore both techniques are probing similar volumes.

In the material irradiated with ps laser pulses above the melting threshold, the Raman beam probes both the region that has undergone melting/rapid solidification and the layer beneath that has only been heated by the laser pulse. The different volumes contributing to the Raman spectrum are schematically shown in Fig. 6 for two different ps pulse fluences below (E_1) and above (E_2) the melting threshold. It was shown in Fig. 4 that the evolution of $\Gamma/2$ for the films on glass exhibits a pronounced minimum for a fluence close to the melting threshold, which is consistent with the fact that the material that has only been heated by the laser beam undergoes a strong relaxation. A similar behavior has been reported earlier for *a*-Si irradiated with ns laser pulses^{7,13,19} where the relaxation rate is observed to increase very rapidly as the melting temperature is approached. However, above the melting threshold, $\Gamma/2$ increases with fluence indicating that the average degree of relaxation of the material probed by the Raman beam decreases as a consequence of the contribution of the upper rapidly solidified layer. Since the layer

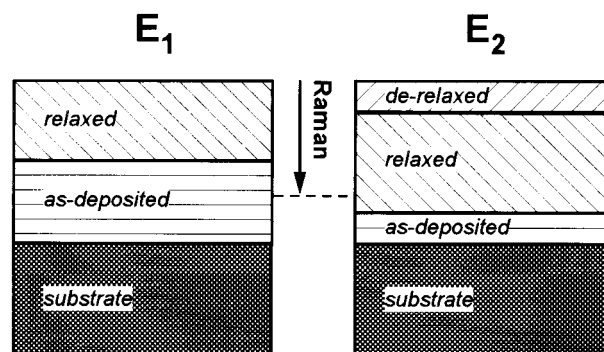


FIG. 6. Scheme of the different contributions to the Raman spectrum in *a*-Ge films irradiated with ps pulses at fluences below (E_1) and above (E_2) the melting threshold. The arrow denotes the depth of material probed by the Raman excitation beam.

beneath, only heated by the laser beam, is strongly relaxed (and thicker) this behavior indicates that the upper rapidly solidified layer should be in a strongly derelaxed state. This interpretation is in agreement with the melting threshold value observed in the material on glass for a ps pulse pretreatment pulse fluence just above the melting threshold (Fig. 3) which is clearly lower than in the as-deposited one, indicating a strong derelaxation.

The increase observed in the evolution of $\Gamma/2$ when the pulse fluence overcomes the melting threshold (Figs. 4 and 5) could alternatively be ascribed to “screening effects,” in which the development of a molten layer at the surface may change the coupling of the laser energy to the bulk of the *a*-Ge layer, reducing the efficiency with which the underlying solid layer relaxes for fluences above the melting threshold. Such screening effects, if any, should also be present upon ns laser pulse irradiation and even more markedly, leading to a smaller degree of relaxation as the fluence is increased above the melting threshold, in contrast to the experimentally observed behavior. It might be also argued that the temperature of the resolidified amorphous layer is very close to the melting point for at least a few tens of ns after solidification, and therefore that the resolidified material should show a degree of relaxation even more pronounced than the one observed for fluences below the melting threshold. However, as discussed above, under ps laser pulses, the reamorphization of the molten layer occurs at a minimum supercooling prior to solidification of ≈ 600 K, i.e., a solidification temperature of about 300 °C which is quite far away from the thermodynamic melting temperature. Thus, we are not in the presence of a “hot liquid” undergoing a slow solidification process in a hot environment, but in the presence of a “extremely cold liquid” undergoing bulk solidification in just a few ns.²⁵ The amount of relaxation that can be expected during the cooling process (≈ 100 ns) starting from a peak temperature of $\approx 300^\circ$ is clearly negligible.⁷

In spite of the discussed depth averaging effects, some further consequences can be obtained from the evolution of $\Gamma/2$ versus the pulse fluence for the films on glass substrates

(Fig. 4). $\Gamma/2$ shows a maximum at a certain fluence above the melting threshold. This indicates that if the fluence is further increased, the “degree of derelaxation” of the upper layer decreases. This is consistent with the evolution of the melting threshold in Fig. 3, since when the pretreatment fluence is increased to a value close to the recalcence (crystallization) threshold, the melting threshold of the pretreated material is observed to increase to a value very close to that of the as-deposited material. As above mentioned, the supercooling prior to solidification is expected to decrease with the fluence of the pretreatment pulse³⁶ consistently with the fact that crystalline phase formation is observed for fluences above $\approx 50 \text{ mJ/cm}^2$. This further supports the existence of a direct relation between the degree of structural relaxation of the rapidly solidified material and the supercooling achieved prior solidification: the lower the supercooling the higher the degree of relaxation.

Finally, the overall evolution of $\Gamma/2$ shown in Fig. 5 for the films on Si irradiated with ps pulses is similar to the one observed in the films on glass (Fig. 4), indicating again the presence of two different volume contributions to the Raman spectra for fluences above the melting threshold: the one of the upper rapidly solidified layer (derelaxed) and the one of the material beneath (relaxed). This result is not surprising since the supercooling expected in the films on Si should be even higher than in the films on glass,²⁵ due to the higher thermal conductivity of the Si substrate. Therefore a material less relaxed than the as-deposited one has to be produced upon rapid solidification. However, the shallower melt depths induced in the films on Si ($\text{max} \approx 10 \text{ nm}$)²⁵ make this derelaxed layer thinner than in the case of films on glass. Since the maximum value of $\Gamma/2$ observed for fluences above the melting threshold for both the films on glass (Fig. 4) and on Si (Fig. 5) is similar ($\approx 24 \text{ cm}^{-1}$), the contribution of the upper derelaxed layer in the films on Si should be stronger, in agreement with the higher supercooling. In addition, this shallower melt depth generates a lower sensitivity of the melting threshold of the films on Si to the state of relaxation of the thinner upper rapidly solidified layer, whose maximum thickness is now well below the skin penetration depth of the irradiation beam. The averaged contribution to the melting threshold of this thinner derelaxed layer and the thicker strongly relaxed layer below is very likely responsible for the weaker decrease of the melting which is observed in the films on Si for increasing pretreatment pulse fluences (Fig. 3).

CONCLUSION

Melting and rapid solidification has been induced in α -Ge films upon pulsed irradiation. It has been shown that a direct relation exists between the degree of relaxation of the rapidly solidified material and the supercooling achieved prior solidification; the lower the supercooling the higher the degree of relaxation. As a consequence, it has been demonstrated that states either more or less relaxed than that of the as-deposited material can be obtained through a proper control of the experimental parameters affecting the supercooling: the duration and fluence of the laser pulse and the thermal conductivity of the substrate.

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